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Deposition and characterization of thin HTS and magnetic perovskite films

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Abstract. The *in-situ* growth and physical properties were investigated of thin films and bilayers of high-temperature superconductors (HTS) $YBa_2Cu_3O_7$ (YBCO) and ferromagnetic (FM) manganites $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) with thicknesses of several tens of nm obtained by magnetron sputtering. Similar twin structures were observed by an optical microscope in areas on the $LaAlO_3$ substrate surface void of films, in areas containing YBCO, in LSMO films, and in YBCO/LCMO bilayers, although the main spatial period of the twin structure seemed to be slightly different in the areas containing the LSMO film. The resistance (and its temperature dependence) of the LCMO films strongly depends on the annealing conditions. The resistance of the LSMO and LCMO films grown on Al_2O_3 substrates decreased as the temperature (*T*) was increased in the lower and higher temperature ranges, and increased as *T* was increased at medium temperatures.

1. Introduction

Perovskite materials demonstrate many interesting properties from both theoretical and applied points of view. Depending on their composition and structural properties, they can behave as dielectrics, conventional metals, high-temperature superconductors (HTS), colossal magnetoresistive materials (CMR), ferroelectric or multiferroic materials [1-3]. Some magnetic perovskites are of particular interest because of their ability to form high-quality epitaxial multilayers of HTS materials [2-7]. The compounds HTS $YBa_2Cu_3O_7$ (YBCO) and ferromagnetic (FM) $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) are considered as very attractive in view of technological applications in electronics, spin sensitive devices and spintronics [2, 3, 8]. The perovskites are multicomponent materials and their growth in a thin film form requires careful optimization processes. The electrical and magnetic characteristics of such thin films depend substantially on the deposition conditions and the

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substrate properties [9-11], as lattice mismatch and defects strongly affect the film properties. The optimization of the deposition process of HTS and FM perovskite films with required characteristics is a challenging task.

The aim of this work is to study the growth conditions and the physical properties of FM and HTS perovskites in the form of both thin films and bilayers of LSMO, LCMO (manganites) and YBCO (HTS).

2. Experimental

Deposition of HTS YBCO and FM LSMO, LCMO films was performed by dual DC magnetron sputtering and single RF magnetron sputtering [12], respectively. The optimal concentration of the sputtering gas was Ar – 50 or 75 % and O_2 – 50 or 25 % for the DC and RF magnetron sputtering systems respectively. The optimal temperature of the substrate during the sputtering process was 780 ^{o}C for these materials. The sputtering process was followed by an annealing procedure of the sample in an O_2 atmosphere at T ~ 500 ^{o}C. The annealing conditions were varied in some of the experiments to find the optimal annealing conditions. To prepare HTS/FM bilayers, YBCO films were sputtered by a DC off-axis double magnetron system on top of RF-magnetron sputtered manganite films. Optical microscopy and atomic force microscopy (AFM) were used to investigate the surfaces of the films. The DC four-probe method and inductive and magneto-optical [7, 13] methods were used to study their electrical and magnetic properties.

3. Results and discussion

3.1. Characteristics of LSMO and HTS YBCO perovskite films grown on LAO substrates

Single-crystal substrates of $LaAlO_3$ (LAO) were used for growing HTS YBCO and ferromagnetic LSMO thin films. The lattice parameter of the LAO substrate (a = 0.3788 nm, pseudocubic) is close to that of LSMO (a = 0.387 nm, cubic) and YBCO (a = 0.382 nm, b = 0.388 nm, orthorhombic); this is why this substrate is suitable for the epitaxial growth of HTS YBCO and FM LSMO thin films. At room temperature, the LAO substrates exhibit a twin structure. It is formed by a ferroelastic (cubic-rhombohedral) transition occurring at ~ 813 K [2, 10] and serves as a template for the film microstructure. In spite of the twin structure, films grown under optimal conditions are characterized by a quite smooth surface (see for example the AFM scan in figure 1 of an LSMO film). Figure 2 shows an optical image (obtained in polarized light) of a film-free area of a LAO substrate (area 1) and of areas containing YBCO (area 2), LSMO (area 3) films and an YBCO/LSMO bilayer (area 4, YBCO is the top layer, LSMO is the bottom layer). It is interesting to note that nearly the same twin structure is observed in all areas of the sample, although the main period of the twin structure seems to be slightly different in the areas containing the LSMO component. Figure 3 shows a magneto-optical micrograph of a HTS YBCO film – a strip (width ~ 0.5 mm), deposited on a LAO substrate. The twin boundaries are not

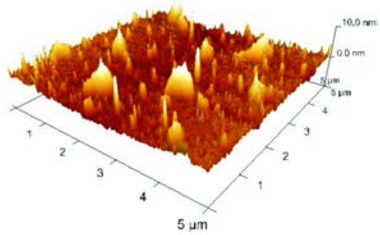

Figure 1. AFM image of a thin LSMO film deposited on a LAO substrate.

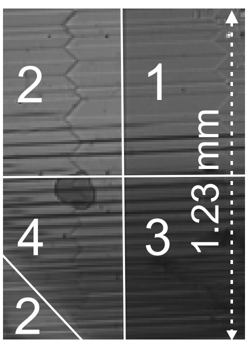

Figure 2. Polarized light optical microscopy image at T = 295 K of an YBCO / LSMO thin film deposited on a LAO substrate:
1 – film-free substrate area; 2 – YBCO film; 3 – LSMO film; 4 – area containing an YBCO/LSMO bilayer.

Figure 3. A trapped magnetic flux distribution pattern in the YBCO strip deposited on a LAO substrate at 77 K.

seen in the strip area (excluding the edge area of the strip and a defective area in the center of the strip). This means that the twin boundaries practically do not affect the “loops” of the electrical current (i.e. the boundaries do not “break” the paths of the electrical current) in the strip induced by the external DC magnetic field. The temperature dependence of the AC response signal, measured in a HTS YBCO thin film and in YBCO/LSMO bilayer (YBCO is the top layer and LSMO is the bottom layer) grown on a LAO substrate, are shown in figure 4. It is seen that the critical temperature of the YBCO thin film is quite high (~ 90 K), which is indicative of its good quality. The critical current density of such films is $J_c > 10^6$ A/cm^2 at T = 77 K. Such critical current densities are typical for high-quality HTS YBCO films of thickness of d > 10 nm, deposited on LAO substrates. The critical temperature of the YBCO film in the bilayer structure is somewhat lower ~ 85 K (figure 4, curve 3). This reduction is partly due to the effect of breaking the Cooper pairs in the HTS film, which leads to a deterioration of the superconducting properties of the film. The pair breaking is caused by spin-polarized charge carriers transported into the HTS layer by diffusion from the FM LSMO layer.

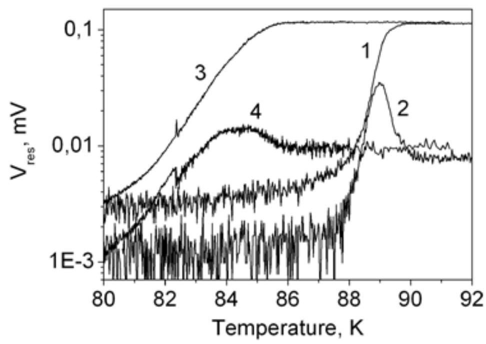

Figure 4. Temperature dependence of the real (1, 3) and imaginary (2, 4) parts of the AC response signal measured in a HTS YBCO single film (1, 2) and a YBCO/LSMO bilayer grown on LAO substrates. The thickness of the YBCO single film is ~ 60 nm, while the thicknesses of the YBCO and LSMO films in the double layer structure are ~ 40 nm and ~ 20 nm, respectively.

3.2. Annealing effect on the resistance of LCMO films grown on LAO and STO substrates

The RF magnetron sputtering process described above was used to prepare $La_{0.7}Ca_{0.3}MnO_3$ (LCMO, a = 0.3868 nm, b = 0.3858 nm, orthorhombic) films on $LaAlO_3$ and $SrTiO_3$ (STO, a = 0.3905 nm, cubic) substrates. The STO and LAO are the single-crystal substrates most commonly used for growing CMR manganite thin films. On the other hand, post-annealing in O_2 is very important for obtaining LCMO thin films with a good quality on such substrates. The temperature dependence of the resistance (curves 1), presented in figures 5 and 6, exhibits a rather insulating character thus indicating an oxygen deficiency in the film. An additional annealing procedure (at a temperature of about 720 °C,

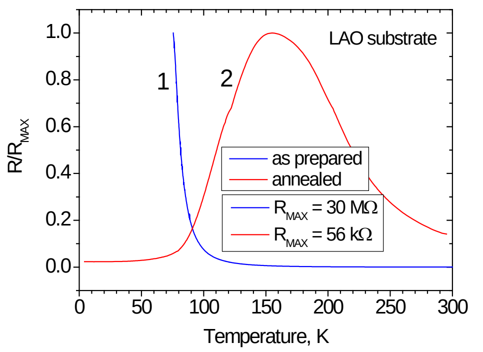

Figure 5. Temperature dependence of the resistance of a LCMO film (thickness ~ 20 nm) deposited on a LAO substrate: 1 – as deposited film; 2 – after annealing.

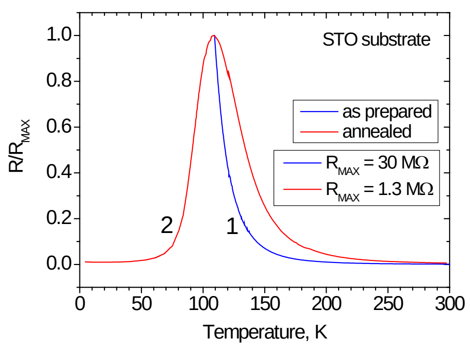

Figure 6. Temperature dependence of the resistance of a LCMO film (thickness ~ 20 nm) deposited on a STO substrate: 1 – as deposited film; 2 – after annealing.

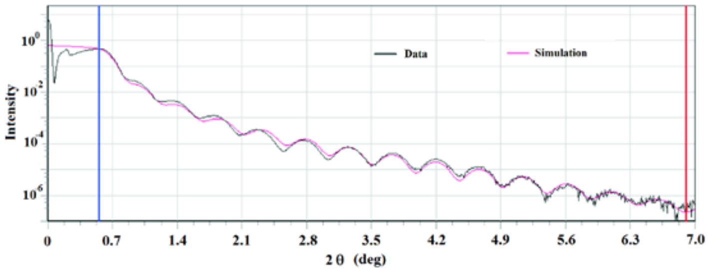

Figure 7. The X-ray reflectivity (Kiessing fringes) of a LCMO film deposited on STO with a simulation of the reflectivity.

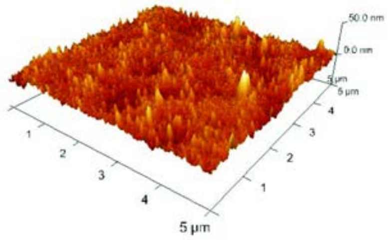

Figure 8. AFM image of a LSMO thin film deposited on an ALO substrate.

oxygen pressure of about 35 mTorr and a duration of 10 minutes) drastically reduces the resistance and produces LCMO films with good CMR and structural properties (figures 5 and 6, curves 2 and figure 7). The X-ray reflectivity of LCMO film on STO is shown in figure 7. The oscillating dependence of the intensity indicates a high structural order, a flat surface and a uniform thickness of the film deposited. The simulation performed yielded an estimated film thickness of 18.16 nm and a surface roughness of 0.313 nm.

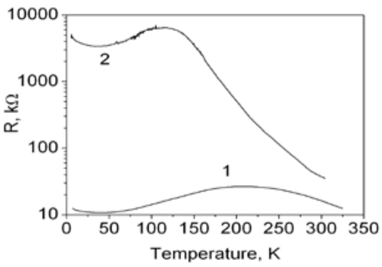

Figure 9. Temperature dependence of the resistance of LSMO (1) and LCMO (2) films deposited on ALO substrates.

3.3. LSMO and LCMO films deposited on ALO substrates

Sapphire (single crystalline Al_2O_3, ALO) is an inexpensive and readily available substrate material. On the other hand, it is not possible to grow epitaxial films of high-T_c superconductors and CMR manganites on ALO substrates because of the significant lattice mismatch and because of the possibility of certain chemical reactions to occur between the film and the substrate. The LSMO and LCMO manganite films in our experiments were directly deposited on ALO substrates by RF magnetron sputtering under the conditions described above. The films thus obtained were of polycrystalline nature and consisted of very small grains with dimensions, possibly, of several tens of nanometers (figure 8). The resistance of these films varied in a wide range as a function of the temperature T (figure 9). The resistance decreased as the temperature was increased in the lower and higher temperature ranges, and increased with the increase of T at medium temperatures (figure 9). A significant change of the resistance and its temperature dependence could be obtained by varying the annealing conditions. Such a behavior of the R vs. T dependence in LSMO and LCMO films grown on ALO substrates could be used to implement sensor-like devices.

4. Conclusions

The *in-situ* growth conditions and the physical properties were investigated of magnetron-sputtered high-temperature superconducting (HTS) $YBa_2Cu_3O_7$ (YBCO), magnetic manganite $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) thin films and bilayers with thicknesses of several tens of nm. Similar twin structures were observed by optical microscopy in the film-free area of the $LaAlO_3$ substrate and in the areas containing YBCO, LSMO films and YBCO/LCMO bilayers, although the main spatial period of the twin structure seemed to be somewhat different in the areas containing LSMO films. Magneto-optical images of the magnetic flux distribution in the YBCO films revealed that the twin structure modulates the critical current density, but does not interrupt the current flow. The resistance (and its temperature dependence) of the LCMO films grown on $LaAlO_3$ and $SrTiO_3$ substrates strongly depends on the annealing conditions. The resistance of the LSMO and LCMO films grown on Al_2O substrates decreased as the temperature was raised in the lower and higher temperatures ranges, and increased as T was raised in the medium temperatures range.

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